Supporting Information

For general methods see ref. 1b. The ^{1}H NMR spectra were recorded in $CDCl_3$ at 200 MHz on a Bruker AM 200 spectrometer.

Typical experimental procedure for competitive glycosylation reaction: To a mixture of **2**α (58.5 mg 0.106 mmol) and **2**β (58.5 mg 0.106 mmol) in 0.9 mL of dry CH_2Cl_2 and 1.6 mL of Et_2O, were added **1b** (82 mg, 0.127 mmol), NIS (29 mg, 0.128 mmol) and 4Å molecular sieves (180 mg). The reaction mixture was cooled at -60°C and 42 µL of a solution of 30 µL of triflic acid in 1 mL of CH_2Cl_2 (0.1 eq.) was added. After 1h the reaction mixture was poured in Et_2O (10 mL) and 2 mL of aq $NaHCO_3$. $NaHSO_3$ was added until decoloration of the organic layer which was then washed with water and dried. After evaporation of the solvent, the residue was dissolved into CH_2Cl_2 and applied on top of a silica gel column (20 g). Elution (Et_2O/pentane/AcOEt, 5/15/1 then 5/15/2 then 5/15/3) gave first a mixture of **4c** and **4d** (93 mg, 67 %) followed by a mixture of unreacted acceptors (56 mg).

2α ^{1}H NMR δ 7.35-7.24 (m, 20 H, H arom.); 5.24 (s, 2H, CH_2Ph); 5.00 (d, 1H, $J_{1,2}$ = 3.4, H-1); 4.80-4.53 (m, 6H, 3 CH_2Ph); 4.40 (br s, 1H, H-5); 4.37 (br s, 1H, H-4); 4.00 (dd, 1H, $J_{2,3}$ = 9.8, $J_{3,4}$ = 3.1, H-3); 3.88 (dd, 1H, $J_{1,2}$ = 3.4, H-2); 2.53 (s, 1H, OH).

$[\alpha]_D^{25}$ = + 59° (c: 3.0, $CHCl_3$). Anal. Calcd for $C_{34}H_{34}O_7$: C, 73.65; H, 6.14. Found: C, 73.40; H, 6.08.

3α ^{1}H NMR δ 5.02 (d, $J_{1,2}$ = 3Hz, H-1); 4.44 (br s, 1H, H-4); 4.40 (br s, 1H, H-5); 3.84 (s, 3H, CH_3O); 3.67-3.57 (m, 2H, H-2, H-3); 3.52, 3.51, 3.47 (3s, 9H, 3 CH_3O).

$[\alpha]_D^{25}$ = + 130° (c 2.0; $CHCl_3$). lit.[3a] + 126° (c 1.9; $CHCl_3$).

3β ^{1}H NMR δ 4.37 (br s, 1H, H-4); 4.20 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1); 4.08 (broad s, 1H, H-5); 3.83, 3.58, 3.57, 3.2 (4 s, 12H, 4 CH_3O); 3.30-3.21 (m, 2H, H-2, H-3).

$[\alpha]_D^{25}$ = - 18° (c 1.0; CH_3OH). lit.[3b] -22° (c 0.9; CH_3OH).

7α ^{1}H NMR δ, 4.72 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1); 3.90 (d, 1H, $J_{5,4}$ = 9.7 Hz, H-5); 3.63 (s, 3H, $COOCH_3$), 3.44, 3.32, 3.29 (3s, 9H, 3 CH_3O) 3.70-3.40 (m, 2H, H-3, H-4); 3.10 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2). ^{13}C NMR δ, 170.68; 98.02; 81.89; 80.85; 71.58; 70.64; 61.14; 58.98; 55.82; 52.65. $[\alpha]_D^{25}$ = + 101.3° (1.3; $CHCl_3$).

7β ^{1}H NMR δ, 4.23 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1); 3.90-3.60 (m, 2H, H-4, H-5); 3.80, 3.62, 3.54, 3.53 (4s, 12H, 4 CH_3O); 3.15 (t, 1H, $J_{3,2}$ = $J_{3,4}$ = 8.76 Hz, H-3); 3.00 (dd, 1H, H-2). ^{13}C NMR δ, 171.17; 104.69; 84.94; 82.90; 74.22; 71.39; 60.98; 60.37; 57.28; 52.68. $[\alpha]_D^{25}$ = - 52.2° (c 1.6; $CHCl_3$).